

## Scientific Objectives of the Critical Viscosity Experiment

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[14 December 1992]

### Summary

In microgravity, the Critical Viscosity Experiment will measure the viscosity of xenon 15 times closer to the critical point than is possible on earth. The results are expected to include the first direct observation of the predicted power-law divergence of viscosity in a pure fluid and they will test calculations of the value of the exponent associated with the divergence. The results, when combined with Zeno's decay-rate data, will strengthen the test of mode coupling theory. Without microgravity viscosity data, the Zeno test will require an extrapolation of existing 1-*g* viscosity data by as much as factor of 100 in reduced temperature. By necessity, the extrapolation would use an incompletely verified theory of viscosity crossover. With the microgravity viscosity data, the reliance on crossover models will be negligible allowing a more reliable extrapolation.

During the past year, new theoretical calculations for the viscosity exponent finally achieved consistency with the best experimental data for pure fluids. This report gives the justification for the proposed microgravity Critical Viscosity Experiment in this new context. This report also combines for the first time the best available light scattering data with our recent viscosity data to demonstrate the current status of tests of mode coupling theory.

### The Viscosity Divergence

This section outlines the theoretical context for the viscosity divergence near the critical point and explains the need, independent of any light scattering data, for its measurement in low gravity. During 1992, the theoretical estimate for the viscosity exponent  $y$  was raised from 0.032 to 0.041 [1], making it consistent with the best 1- $g$  viscosity measurements on pure fluids [2]. However, demonstrating this consistency requires the use of an interpolating "crossover" function, defined below, and an accounting for the complications due to density stratification of the test fluids in the Earth's gravitational field.

Near liquid-vapor and liquid-liquid critical points the most rigorous prediction, which comes from dynamic scaling theory, is that, in the asymptotic limit where critical fluctuations dominate the fluid's properties, the viscosity  $\eta$  will diverge as a power  $x_\eta$  of the correlation length  $\xi$ , namely

$$\eta \propto \xi^{-x_\eta} \propto (T - T_c)^{-y}. \quad (1)$$

Thus the temperature dependence of the viscosity is characterized by the exponent  $y \equiv \nu x_\eta$ . However, this asymptotic limit, in which the critical contribution to viscosity greatly exceeds the noncritical background contribution, occurs only within some tens of nanokelvin of the critical temperature  $T_c$ . Thus the asymptotic limit is experimentally unobservable.

The less rigorous mode coupling theory addresses the viscosity increase which is observable near  $T_c$  in terms of the noncritical viscosity  $\eta_0$  and a universal function  $H(\xi)$  [3] which describes the crossover between the purely noncritical and purely critical regions through the following ansatz:

$$\eta = \eta_0(\rho, T) \exp[x_\eta H(\xi)]. \quad (2)$$

There is no accurate theory for the noncritical viscosity  $\eta_0(\rho, T)$  for either pure fluids or binary liquid mixtures. However, for tests of theory, a simple pure fluid such as xenon has two advantages. First, the dependencies of  $\eta_0(\rho, T)$  on density  $\rho$  and temperature  $T$  are weak compared with the dependencies of  $\eta_0(x, T)$  on mole fraction  $x$  and temperature for binary liquids. For xenon, the temperature dependence is indistinguishable from the well-understood dilute gas behavior  $\eta_0(0, T)$ . The second advantage of pure fluids such as

xenon is the availability of the parameter  $q_C$  needed in the crossover function  $H(\xi)$ .  $H(\xi)$  depends on both density and temperature through the correlation length  $\xi$  and it incorporates two fluid-dependent wave vectors  $q_C$  and  $q_D$ . The wave vector  $q_C$  has not been determined for any binary liquids. The wave vector  $q_D$  represents the effective cutoff used in a mode coupling integral over momentum space. It is a free parameter related to the amplitude of the viscosity divergence, and it cannot be measured independently.

In effect,  $H(\xi)$  is an interpolation function chosen to have the correct limiting forms both near and far from the critical point. Although Sengers and co-workers have used  $H(\xi)$  in correlations of transport data [4],  $H(\xi)$  has not been tested for pure fluids in the region where  $\eta$  exhibits power-law behavior because that region is not accessible on earth.

As shown in Fig. 1, density stratification near the critical point of a 0.7 mm high sample of xenon limited the viscosity increase at reduced temperatures below  $\epsilon$  near  $3 \times 10^{-5}$ . Although the theory and parameters for the equilibrium stratification profile are well known, stratification complicates the hydrodynamics and obscures the critical enhancement. The power-law behavior in Eq. (1) that is expected at reduced temperatures less than  $1 \times 10^{-4}$  has never been observed in a pure fluid.

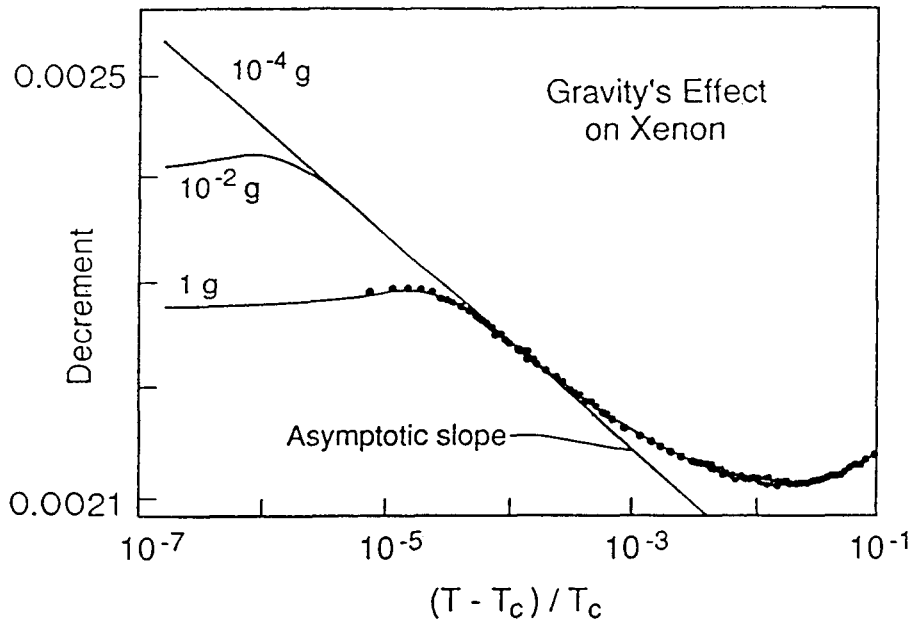


Fig. 1. Gravity's effect on viscosity measurements near the critical point of xenon. The curve labeled "1 g" is a fit to the decrement data obtained from a 0.7 mm high torsion oscillator [2]. (The decrement is approximately proportional to the square root of viscosity.) The two upper curves show the results expected if the measurement were repeated in reduced gravity. Because the asymptotic region is inaccessible in 1 g, the extrapolation of the viscosity towards  $T_c$  is sensitive to the theory of the crossover between the noncritical and critical regions.

The power-law behavior predicted by dynamic scaling and the theoretical value of the associated exponent  $x_\eta$  would be tested by an unambiguous observation of a divergence of the form of Eq. (1). However, as Fig. (1) shows, the crossover region appears to end at the same reduced temperature where significant gravity effects begin, at about  $\epsilon = 10^{-4}$ . Thus the best 1- $g$  viscosity measurements can test only the combination of the theories for the exponent  $x_\eta$  and the crossover function  $H(\xi)$ .

Although our measurements on the pure fluids xenon and carbon dioxide are consistent with present crossover theory, for binary liquids, where the power-law divergence is directly observable, viscosity measurements are not consistent with crossover theory [5]. Should the additional xenon data from the flight experiment also prove inconsistent with crossover theory, the data would still be valid for the comparison with Zeno's light scattering data. Furthermore, there would then be a strong motivation to improve the theory for the viscosity divergence, perhaps at several levels. First, various approximations, though presently believed to be small, could be eliminated. These include neglect of the frequency dependence of viscosity, neglect of effects of the order of the inverse heat capacity ratio  $C_v/C_p$ , neglect of vertex corrections, assumption of Ornstein-Zernike correlations near  $T_c$ , and use of the same cutoff wave vector  $q_D$  for both viscosity and thermal conductivity. Second, although mode coupling theory predicts only a logarithmic divergence of viscosity, it has not been extended even enough to verify that the next term is consistent with an eventual power-law divergence. Such an extension would test the ansatz of Eq. (2).

To summarize, in microgravity the power-law divergence of viscosity could be directly observed in a pure fluid for the first time. Crossover theory, which agrees with 1- $g$  pure fluid data, could also then be tested at a level presently available only for binary liquids, for which the current theory fails.

### Relationship Between Viscosity and Light Scattering

Mode coupling theory predicts a consistency relationship between viscosity data and dynamic light scattering data. Dynamic scaling and the main outline of mode coupling theory have been accepted as experimentally verified since the 1973 publication of Swinney and Henry [6], who found consistency to within 20 % for a variety of pure fluids, including xenon. Since then, the best improvement in precision was made by Burstyn et al. [7], who measured and compared against theory fluctuation decay rates in the binary liquid nitroethane + 3-methylpentane to within  $\pm 1$  %. A similar comparison using a pure fluid has not been achieved because of the inability to go close to  $T_c$  without encountering problems due to density stratification.

In what follows we use the best available light scattering and viscosity measurements for xenon to: (1) update testing of mode coupling in a pure fluid, (2) show present limits on light scattering measurements in 1-g, and (3) demonstrate the procedure that would be used for comparison of the improved data resulting from a flight experiment. These light scattering data were first obtained and used to test mode coupling by Güttinger and Cannell [8]. They used a xenon viscosity correlation based on the measurements of Strumpf et al. [9], which were limited by viscoelastic effects because the viscosity was measured at 39 kHz. We re-analyzed the Güttinger–Cannell decay rate data with the improved formalism of Burstyn et al. and our recent 1 Hz viscosity data. The present re-analysis demonstrates the consistency of mode coupling theory with the pure fluid and binary liquid mixture data (mentioned above) at large values of  $q\xi$ ; however, it does not remove the inconsistencies at small values of  $q\xi$ . Moreover, this test of mode coupling is not complete because of uncertainties in making background corrections far from  $T_c$  and the limitations imposed by gravitational stratification of the samples close to  $T_c$ .

The fundamental prediction of dynamic scaling is that a fluid's dynamic behavior is governed by the fluctuation decay rate  $\Gamma^c$ , which depends only on the wave vector  $q$  and the correlation length  $\xi$  according to

$$\Gamma^c = q^z f(x) , \quad (3)$$

where  $z$  is the dynamic scaling exponent and  $f(x)$  depends on  $\xi$  only through the dimensionless parameter  $x \equiv q\xi$ . Mode coupling gives explicit expressions for  $f(x)$ . For example, with various approximations, including neglect of the frequency and wave vector

dependence of viscosity, the critical contribution to the decay rate is

$$\Gamma^c = \frac{k_B T}{6\pi\eta\xi} \Omega_K(x), \quad (4)$$

where  $k_B$  is Boltzmann's constant and

$$\Omega_K(x) = \left[ \frac{3}{4x^2} \right] [1 + x^2 + (x^3 - x^{-1})\tan^{-1}(x)]. \quad (5)$$

In practice, the observed decay rate is assumed to be the sum

$$\Gamma = \Gamma^b + \Gamma^c \quad (6)$$

of a background contribution  $\Gamma^b$  and the critical contribution  $\Gamma^c$ . Although the ratio  $\Gamma^b/\Gamma^c$  is typically less than 10 % near  $T_c$ , it can be of order unity for pure fluids 3 K above  $T_c$ , thereby obscuring tests of mode coupling at small values of  $q\xi$ .

The most precise test of the mode coupling theory for the relationship between viscosity data and light scattering data was made by Burstyn, Sengers, Bhattacharjee, and Ferrell [7] in the binary liquid nitroethane + 3-methylpentane. Instead of numerically solving the coupled integral equations for viscosity and decay rate, they devised an analytic improvement to Eq. (4)

$$\Gamma^c = \frac{Rk_B T}{6\pi\eta\xi} \Omega_K(x) [1 + b^2 x^2]^{x\eta/2}, \quad (7)$$

with the additional universal parameters  $R$  and  $b$ . To compare their data to Eq. (7), they first subtracted the background  $\Gamma^b$ , which depends on the wave vector  $q_C$ . Although lack of an independent measurement forced them to estimate  $q_C$  heuristically, they excluded data where the background contributed more than 1 % to the total decay rate. Fig. (2a) shows their data, normalized according to

$$D^* \equiv \left[ \frac{6\pi\eta\xi}{k_B T} \right] \frac{\Gamma^c}{q^2} \quad (8)$$

Fig. (2b) shows that deviations from the universal function  $D^*$ , obtained with the free parameters

$$R = 1.01 \pm 0.04 \text{ and } b = 0.5 \pm 0.2 \text{ (binary liquid),} \quad (9)$$

are within  $\pm 1\%$ . The above error bars for  $R$  and  $b$  quoted by Burstyn et al. are very conservative, reflecting for example, the effects of a 20 % uncertainty in the viscosity exponent. The precision with which they determined  $R$  was approximately 0.1 %, although the scatter of the data that was averaged is on the order of  $\pm 1\%$ .

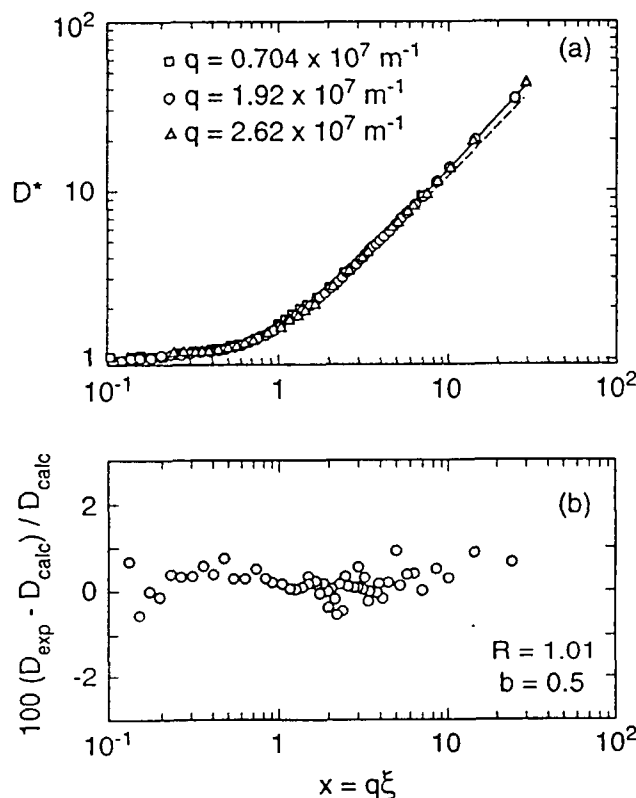


Fig. 2a. Fluctuation decay rate data obtained by Burstyn et al. [7] in the binary liquid nitroethane + 3-methylpentane. The data are plotted in the reduced form

$$D^* \equiv \frac{6\pi\eta\xi}{k_B T} \frac{(\Gamma - \Gamma^b)}{q^2}$$

to eliminate explicit dependence on the correlation length. The solid curve is Eq. (7) with  $R = 1.01$  and  $b = 0.5$ . The dashed curve results if  $b \equiv 0$ .

Fig. 2b. Deviations of the binary liquid data from Eq. (7) as a function of the dimensionless scaling parameter  $q\xi$ . The best fit values are  $R = 1.01$  and  $b = 0.5$ .

Pure fluids have not been tested to comparable accuracy. The best test so far published was made by Güttinger and Cannell [8] on xenon. In their publication,

Güttinger and Cannell used the same formalism and viscosity correlation used by Swinney and Henry [9]. Here we compare their data using both the improved scaling function devised by Burstyn et al., Eq. (7), and our recent viscosity data. Their data are shown in Fig. (3) and some details of our analysis are described in the Appendix.

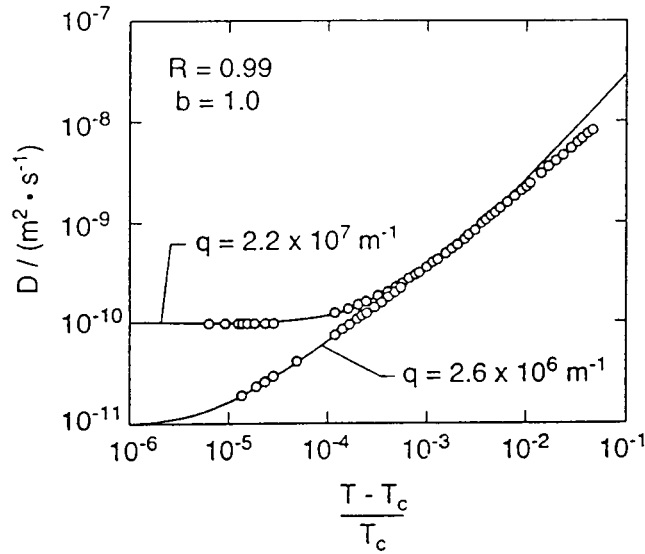


Fig. 3. Güttinger and Cannell's data for the diffusivity of xenon as a function of reduced temperature. The curves use both Eq. (7) with  $R = 0.99$  and  $b = 1.0$  and a background correction.

Fig. (4a) shows the normalized critical diffusion  $D^*$  for xenon. The large  $q$  data extend to  $q\xi = 7$  and the small  $q$  data extend only to  $q\xi = 0.6$ . In contrast, the binary liquid data of Fig. (2a) includes data from at least two values of  $q$  spanning the range  $0.2 < q\xi < 30$ . The data for xenon of Fig. (4b), calculated using the same binary liquid values  $R = 1.01$  and  $b = 0.5$ , deviate from Eq. (7) by 5–15 % at small values of  $q\xi$ . If the parameters  $R$  and  $b$  are assigned the values

$$R = 0.99 \quad \text{and} \quad b = 1.0 \quad (\text{pure fluid}), \quad (10)$$

the deviations at large  $q\xi$  are reduced to the experimental precision of  $\pm 2$  %, as shown in Fig. (4c). However, the inconsistencies for  $q\xi < 0.3$  become worse.

Although the parameter pairs Eqs. (9) and (10) differ, they lead to the same values of the asymptotic limit of Eq. (7). The limit is:

$$Rb^x \eta = (1.01)(0.5^{0.063}) \simeq (0.99)(1.0^{0.064}) \simeq 0.99. \quad (11)$$



Thus the limit is the same for the xenon data and the (nitroethane + 3-methylpentane) data. Consistency between these two data sets may approach 2 %, given the combined inaccuracies of the viscosities ( $\Delta\eta = 1.5$  % for nitroethane + 3-methylpentane [7] and  $\Delta\eta = 0.8$  % for xenon [2]). However, the inconsistencies are much larger at small values of  $q\xi$ . The apparent inconsistency between data obtained at different values of  $q$  may result from an inadequate theory for the background decay rate  $\Gamma^b$ .

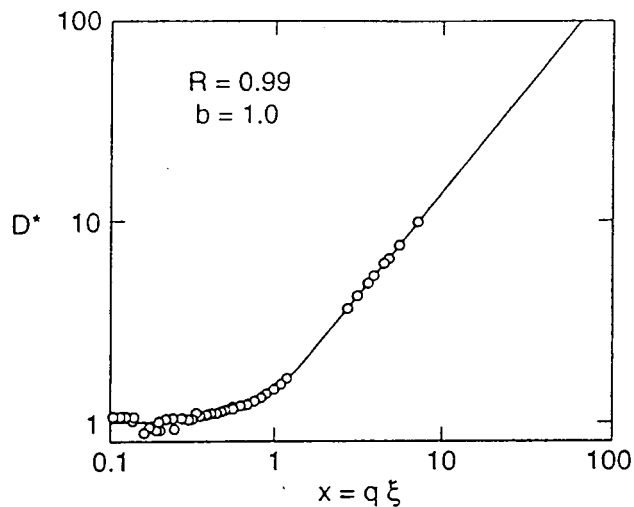


Fig. 4a. The xenon data of Fig. (3) scaled as in Fig. (2a) for the binary liquid. Density stratification limited the acquisition of small- $q$  data at large values of  $q\xi$ .

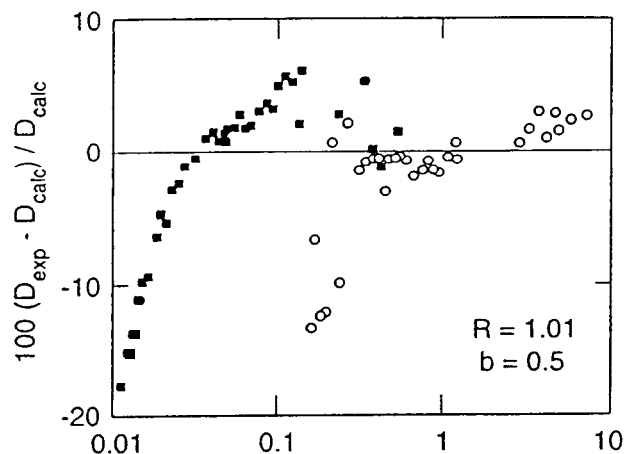


Fig. 4b. Deviations of the xenon data from Eq. (7) as a function of the dimensionless scaling parameter  $q\xi$ . The values of the parameters  $R$  and  $b$  are chosen to be the same as for the binary liquid nitroethane + 3-methylpentane.

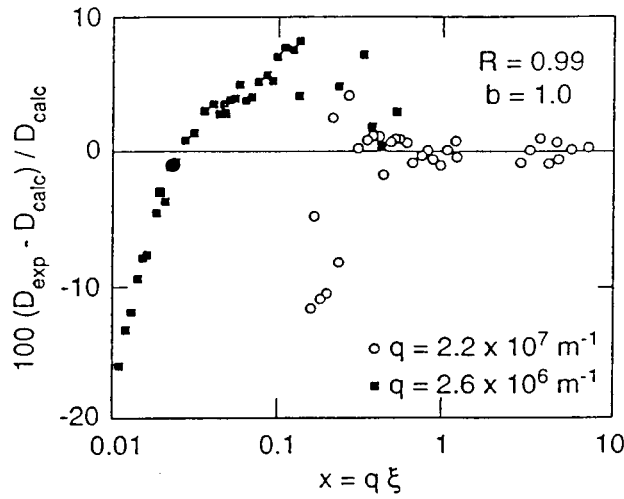


Fig. 4c. Deviations of the xenon data from Eq. (7) resulting from the values  $R = 0.99$  and  $b = 1.0$  chosen to minimize deviations at large  $q\xi$ . The inconsistencies seen in Fig. (4b) at small  $q\xi$  remain.

Improvements are needed in two places. First, for  $q\xi < 0.3$  (far from  $T_c$ ), the 5–15 % discrepancies in the xenon fluctuation decay rates, both between different values of  $q$  and between experiment and theory need to be resolved. The resolution will require either better theoretical characterization of the background decay rate  $\Gamma^b$ , or new data in this region (accessible in 1 *g*), or possibly both. New data at 1 *g* should be taken using Zeno techniques as soon as possible.

Second, new data at small  $q$  are needed at  $1 < q\xi < 30$ , where scaling theory predicts the  $q$ -dependence

$$\Gamma^c \sim q^z, \quad (12)$$

of the decay rate at large  $q\xi$ . Reduction of the uncertain background correction  $\Gamma^b$  requires measurements at small  $q$  (low angles). Achieving large  $q\xi$  then requires large  $\xi$ , which in turn requires temperatures close to  $T_c$ . Stratification problems prevented Güttinger and Cannell from approaching  $T_c$  closer than 3 mK to verify Eq. (12). Zeno will meet this need for the first time by obtaining data at  $12^\circ$  and  $168^\circ$  at  $\epsilon \geq 3 \times 10^{-7}$  (i.e. to within 0.1 mK of  $T_c$ ).

To summarize, mode coupling's predictions of fluctuation decay rates is incompletely tested in pure fluids. At small values of  $q\xi$  the discrepancies are 5–15 % and will require more ground-based work. At large values of  $q\xi$  verification of Eq. (12) must await the results of Zeno. In both regions, viscosity and light scattering data accurate to

about 1 % are needed to test mode coupling to an accuracy already achieved in the binary liquid nitroethane + 3-methylpentane. Although the available 1-*g* viscosity data can be extrapolated to  $\epsilon = 3 \times 10^{-7}$  with such precision, for the reasons stated in the previous section, the theoretical reliability of this extrapolation is unproven. New viscosity data obtained closer to  $T_c$  would eliminate this ambiguity and ensure the accuracy of comparisons of theory against Zeno's data.

#### Acknowledgements

We thank D.S. Cannell for useful comments and the data of Ref. 8. We thank R.W. Gammon, J. V. Sengers, and A. Wilkinson for providing helpful suggestions and for critically reading this report.

### Appendix

Testing of Eq. (7) requires three sets of data, each a function of reduced temperature. These are the correlation length, obtained from static light scattering measurements, the fluctuation decay rate, or inverse correlation time, obtained from dynamic light scattering measurements, and the viscosity. In the above comparison we relied on light scattering data provided by D.S. Cannell and on our own viscosity measurements.

For the correlation length measurements we used [8] the empirical formula:

$$\xi = (1.93 \times 10^{-10} \text{ m}) \epsilon^{-0.62} . \quad (13)$$

The exponent 0.62 differs slightly from the expected value  $\nu = 0.63$ . Presumably, the difference results from corrections to scaling. Equation (13) cannot be reliably extrapolated outside the measured range; however, our spot checks verified Eq. (13) accurately fits the data.

For the viscosity, we used the same crossover formalism and fit parameters used to describe our xenon viscosity data [2].

The fluctuation decay rate data, which have more scatter than the other two data sets, were used directly; they were not fitted by an empirical function.

We have already described the influence of the viscosity data on the interpretation of light scattering data close to  $T_c$  [2]. One consequence is that, in the limit of large  $q\xi$ , the critical diffusivity is

$$D_c = \left[ \frac{Rk_B T q}{16 \eta_0} \right] \left[ \frac{b q \xi_0}{Q_0 \xi_0} \right]^{y/\nu} , \quad (14)$$

The directly measured fluid-dependent parameters are the background viscosity  $\eta_0$ , the correlation length  $\xi_0$ , and the dimensionless product  $Q_0 \xi_0$ .

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